

**U.S. DEPARTMENT OF COMMERCE
National Technical Information Service**

PB-268 954

**Evaluation of the Technological Feasibility, and
Cost of Selected Control Alternatives Necessary to
Meet the Proposed Ohio SO₂ Regulations for Industrial
Boilers and Processes. Vol. I. Youngston Sheet and Tube
Company, Campbell Works - Coke Oven Gas Desulfurization**

GCA Corp, Bedford, Mass. GCA Technology Div.

Prepared for

**Environmental Protection Agency, Chicago, Ill. Air and Hazardous Materials
Div.**

Jun 76

PB 268 954

Volume I

YOUNGSTOWN SHEET AND TUBE COMPANY,
CAMPBELL WORKS —
COKE OVEN GAS DESULFURIZATION

GCA/TECHNOLOGY DIVISION 

REPRODUCED BY
**NATIONAL TECHNICAL
INFORMATION SERVICE**
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EVALUATION OF THE TECHNOLOGICAL FEASIBILITY, AND
COST OF SELECTED CONTROL ALTERNATIVES
NECESSARY TO MEET THE PROPOSED
OHIO SO₂ REGULATIONS FOR
INDUSTRIAL BOILERS AND PROCESSES

FINAL REPORT

Contract No. 68-01-3155
Task Order No. 4

June 1976

Volume I

YOUNGSTOWN SHEET AND TUBE COMPANY,
CAMPBELL WORKS —
COKE OVEN GAS DESULFURIZATION

by

Robert R. Hall
Walter T. Stanley
James Sahagian

GCA CORPORATION
GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts

EPA Contract Officer

Wayne E. Pearson
Air Policy Branch, A&HMD
Environmental Protection Agency, Region V
230 South Dearborn Street
Chicago, Illinois 60604

U.S. ENVIRONMENTAL PROTECTION AGENCY
Division of Stationary Source Enforcement
Washington, D.C. 20460

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-905/2-76-005-a		2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Evaluation of the Technological Feasibility and Cost of Selected Alternatives Necessary to Meet the Proposed Ohio SO ₂ Regulations for Industrial Boilers and Processes.		5. REPORT DATE August 1976	
7. AUTHOR(S) Volume I Robert R. Hall, Walter T. Stanley, James Sahagian		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS GCA Corporation GCA/Thchnology Division Bedford, Massachusetts		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Air Programs Branch, A&H/MD Environmental Protection Agency, Region V 230 S. Dearborn Chicago, Illinois 60604		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. 68-01-3155 Task Order No. 4	
		13. TYPE OF REPORT AND PERIOD COVERED Final	
		14. SPONSORING AGENCY CODE 905/SC	
15. SUPPLEMENTARY NOTES One of 9 documents supporting sulfur dioxide control strategy for the State of Ohio Technical Support Document Vol. I and II EPA 905/2-76-002			
16. ABSTRACT This report presents an evaluation by the GCA Corporation, GCA/TEchnology Division, of the technological feasibility and cost of complying with the proposed Ohio sulfur dioxide regulation (40 FR 52410, November 10, 1975) at Youngstown Sheet and Tube's Campbell Works. The final USEPA Sulfur Dioxide Strategy for the State of Ohio Technical Support Documents, Vol. I and II, (EPA 905/2-76-002) may be obtained from NTIS. The Campbell Works was an example of a by-product coke over facility. After collecting necessary site and source specific data by means of a plant visit, the technical feasibility of the vacuum carbonate, Dravo Firma, Carl Still, Sulfiban and Holmes Stretford processes were evaluated. Capital and operating costs are presented for the latter three systems.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Byproducts Coking Cost Estimates Desulfurization Sulfur Dioxide	Control Strategy Coke Ovens Ohio Youngstown Sheet and Tube	13B 13H	
19. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES 47	
	20. SECURITY CLASS (This page)	22. PRICE A03 - A01	

EVALUATION OF THE TECHNICAL FEASIBILITY AND COST OF SELECTED CONTROL
ALTERNATIVES NECESSARY TO MEET THE PROPOSED OHIO SO₂ REGULATIONS
FOR INDUSTRIAL BOILERS AND PROCESSES

FINAL REPORT

JUNE 1976

VOLUME I

YOUNGSTOWN SHEET AND TUBE COMPANY

CAMPBELL WORKS - COKE OVEN

GAS DESULFURIZATION

Report No. GCA-TR-76-14-G(1)

ERRATA

Page 1, paragraph 2, line 6	change "20 to 30" to "30 to 40"
Page 6, paragraph 3, line 3	change "464 grains (H ₂ S equivalent)/100 scf" to "464 grains H ₂ S/100 scf and an unknown amount of organic sulfur."
Page 12, paragraph 2, line 1	change "eight" to "nine"
Page 12, paragraph 2, line 2	change "three" to "two"
Page 12, paragraph 2, line 5	change "322,000" to "417,000"
Page 12, paragraph 2, line 7	change "1/3" to "40 percent"
Page 13, table 12, line 7	change "40" to "300"
Page 14, paragraph 2, line 3	change "450" to "710"
Page 15, footnote	change "1948" to "27125" and "Oklahoma City, Oklahoma 73101" to "Houston, Texas 77024"
Page 20, paragraph 2, line 8	change "usually 5 to 10 grains/scf" to "usually 5 to 10 grains scf but ranging to 25 grains/scf"
Page 30, paragraph 1, line 5	change "\$0.18-\$0.20" to "\$0.23-\$0.26"
Page 30, paragraph 3, line 5	change "II-5" to "7"

ib

GCA/TECHNOLOGY DIVISION ●●▲

This Final Report was furnished to the Environmental Protection Agency by the GCA Corporation, GCA/Technology Division, Bedford, Massachusetts 01730, in fulfillment of Contract No. 68-01-3155, Task Order No. 4. The opinions, findings, and conclusions expressed are those of the authors and not necessarily those of the Environmental Protection Agency or of the cooperating agencies. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

ABSTRACT

The results of an evaluation of the technical feasibility, and cost, of coke oven gas desulfurization to meet the proposed Ohio emission limit of 50 grains H_2S equivalent/100 scf are presented in this report. Youngstown Sheet and Tube (YS&T) Company, Campbell Works, Struthers, Ohio was used as an example site and the costs presented are specific to YS&T. The technical feasibility of the Vacuum Carbonate, Dravo Firma Carl Still, Sulfiban and Holmes Stretford processes were evaluated. Capital and operating costs are presented for the latter three systems.

CONTENTS

	<u>Page</u>
Abstract	iii
List of Figures	v
List of Tables	vi
Acknowledgments	vii
<u>Sections</u>	
I Summary and Conclusions	1
II Process and Site Description	3
III Control Technology for Coke Oven Gas Desulfurization	12
IV Cost of Control Systems	29
V References	36

FIGURES

<u>No.</u>		<u>Page</u>
1	Youngstown Sheet and Tube Company, Campbell Works, By-Product Coke Plant	5
2	COG Desulfurization and Sulfur Recovery Required to Meet the Proposed 50 Grains H ₂ S/100 scf Standard Based on an Inlet Concentration of 464 Grains H ₂ S/100 scf	8
3	YS&T By-Product Plant Site Layout Diagram Indicating Available Space for COG Desulfurization	11
4	Process Flowsheet: Vacuum Carbonate Process Based on 60 Million scf/day COG and 93 Percent Sulfur Collec- tion Efficiency	15
5	Process Flowsheet: Sulfiban Process Including Claus Plant Sulfur Recovery	17
6	Process Flowsheet: Dravo-Firma Carl Still Process for COG Desulfurization (Basis: 35 to 50 Grain H ₂ S/100 scf Outlet Loading)	21
7	Process Flowsheet: The Stretford Process	26

TABLES

<u>No.</u>		<u>Page</u>
1	Typical Yields of Coke Plant Products per Ton of Coal	4
2	Inventory of U.S. Coke Oven Gas Desulfurization Plants, May 1976	13
3	Coke Oven Gas Desulfurization as a Function of Amine Circulation Rate	18
4	Typical Acid Gas Compositions Across Cyanide Destruct Reactor for Various Absorption Processes	23
5	Utility, Material, and Labor Requirements for 60×10^6 scfd COG Desulfurization Systems	31
6	Utility, Material, and Labor Costs for 60×10^6 scfd COG Desulfurization Systems at YS&T, \$/Day	33
7	Costs for 60×10^6 scfd COG Desulfurization Systems at YS&T $\$10^3$, May 1976	35

ACKNOWLEDGMENTS

The assistance of Mr. Wayne E. Pearson, Project Officer, and Mr. Thomas Blaszak, U.S. Environmental Protection Agency, Air Policy Branch, Region V, Chicago, Illinois is gratefully acknowledged.

SECTION I

SUMMARY AND CONCLUSIONS

Youngstown Sheet and Tube (YS&T) Campbell Works was selected as an example by-product coke oven facility. The technical feasibility, and cost, of meeting the proposed regulation limiting sulfur dioxide emissions from coke oven gas to 50 grains H_2S equivalent/100 scf was investigated with regard to the YS&T facility.

Five coke oven gas desulfurization systems, Sulfiban, Vacuum Carbonate, Firma Carl Still, Stretford, and Diamox are commercially available and are technically capable of meeting the proposed regulations. The Sulfiban, Vacuum Carbonate and Firma Carl Still systems are currently operating, under construction or committed to be constructed at by-product coke ovens representing 20 to 30 percent of U.S. capacity.

The Stretford system is currently used at Dominion Foundry in Canada and could be used at other plants pending demonstration of the Holmes liquid effluent control system and acceptance by industry.

Capital, operating and annualized cost were derived for the Sulfiban, Dravo-Firma Carl Still and the Holmes-Stretford systems for application to the YS&T by-product coking operation. The capital costs of installed battery limit plants for the three systems were \$10, \$9.5 and \$7.5 million respectively based on vendor estimates. The net operating costs for the Holmes-Stretford system were also low, \$862,000/year compared to \$1,410,000/year and \$1,290,000 for the Sulfiban and Dravo Firma Carl Still systems. Annualized costs including cost of capital, federal income tax, depreciation

and net operating cost ranged from \$1,960,000/year to \$2,900,000/year. On the basis of sulfur removed these annualized control cost range from \$0.15/lb S to \$0.24/lb S removed. All costs represent May 1976 prices.

SECTION II

PROCESS AND SITE DESCRIPTION

Youngstown Sheet and Tube (YS&T) Company, Campbell Works was visited on 6 April 1976. This facility is located near Youngstown in Struthers, Ohio, Mahoning County, on the Mahoning River in a small valley. The Campbell Works plant is an average size integrated iron and steel plant. About 5,600 tons/day of 1.5 percent sulfur coal are used to produce metallurgical coke by the by-product coking process. The purpose of the plant visit was to collect site and process specific data necessary to determine the technical feasibility and cost of complying with the proposed regulation for control of SO₂ emissions from coke oven gas. Other processes at YS&T were not investigated.

Mr. T. M. Hendrickson, director of environmental control and Mr. C. G. Krichbaum, general foreman of the by-product coke plant represented YS&T. The by-product coke facilities were inspected, process data and site layout diagrams were provided by YS&T and operations were discussed.

The Campbell Works by-product coke plant consists of three coke oven batteries of 76 ovens each and the associated by-product recovery facility. The facility began coking operations in 1917. In 1954, 1955, and 1958, the batteries were razed and rebuilt and then in 1972 and 1973 they were refurbished. Estimated life of the structures is approximately 40 years.

Design capacity of the coke plant is 5600 tons coal consumed/day. Seventy percent of this coal is converted to metallurgical coke. The primary use of the coke is in blast furnace production of pig iron. The remaining

30 percent of the coal charge is evolved as mixed gases and vapors referred to as coke oven gas (COG). Raw coke oven gas is treated in the by-product recovery facility for removal of tar, ammonia, and light oil. The treated COG has a heating value of about 500 Btu/scf and is used as fuel for firing the coke ovens, boilers, and process heaters in the steel plant. A flow diagram of the Youngstown Sheet and Tube Company by-product coke plant is presented in Figure 1.

Exhausters and boosters are employed to maintain a relatively fixed suction pressure. Raw coke oven gas from the batteries is collected in a common main, then flows through primary cooling towers where approximately 98 percent of the tar is washed out. The COG is drawn from these towers by an exhauster into rod and cylinder tar precipitators where the remaining tar is removed. Next the COG is reheated and treated in the ammonia saturators where ammonia is absorbed from the gas stream to produce ammonium sulfate. Finally, the COG is cooled in the final coolers and scrubbed free of naphthalene in the light oil scrubbers. The final coolers are direct contact water coolers and remove part of the HCN and other acid gases present in the COG. Typical yields of products from by-product coking are presented in Table 1.

Table 1. TYPICAL YIELDS OF COKE PLANT PRODUCTS PER TON OF COAL¹

Blast furnace coke and coke breeze	1400 lb
Coke oven gas	10,500 scf
Tar	10 gal
Ammonium sulfate	25 lb
Waste ammonia liquor	25 gal
Light oil	3 gal



Figure 1. Youngstown Sheet and Tube Company, Campbell Works, by-product coke plant

Approximately 40 percent of the clean coke oven gas is used to under-fire the coke ovens. The remainder of the COG is driven by boosters to the steel plant where it is burned in slab reheaters and ingot soaking pits in cold rolling operations. Any COG not burned in the coke ovens or process heaters is used as an auxiliary boiler fuel.

The coke oven batteries are designed to operate 24 hours per day with an 18 hour coking cycle. Each cycle consumes 4200 tons of coal and produces 2,940 tons of blast furnace coke. The by-products recovery plant is designed to process 60 million scf of COG per day. At the present time, the coke ovens are being operated on a 19 hour coking cycle, consuming 5,300 tons/day of coal and producing about 55.7 million scf per day of COG. Oven pushing and loading operations are scheduled at evenly spaced time intervals, but, fluctuations in the coal loading rate normally occur due to shift changes and regular maintenance. Also, the quantity of COG evolved per ton of coal can range from 9,500 scf to 11,500 scf. As a result of these fluctuations, the gas flow rate to the by-product recovery plant can vary up to 20 percent from the mean as shown in flow chart recordings collected by GCA.

Based upon chemical analyses obtained from Youngstown Sheet and Tube Company during the site visit, the mean sulfur content of the coke oven gas is 464 grains (H_2S equivalent)/100 scf. This sulfur originates from the coal charged to the coke ovens which contains 1.5 percent sulfur by weight.

Burning coke oven gas with this sulfur content would violate S54.1881(b)(12) of the proposed Ohio SO_2 emission control regulations. The regulation states the following:

No owner or operator of a by-product coke oven shall cause or permit the combustion of by-product coke oven gas containing a total sulfur content expressed as hydrogen sulfide (H_2S) in excess of 50 grains H_2S per dry standard 100 cubic feet of coke oven gas. Included in the permitted concentration of H_2S are emissions of sulfur dioxide emitted as off gas from the sulfur recovery system operated in conjunction with the sulfur removal equipment, and sulfur dioxide emitted due to the mixing, flaring, or distribution of by-product coke oven gas.

Thus for a plant which burns 60 million scf of coke oven gas per day, total sulfur emissions expressed as H_2S must not exceed 4,286 lb/day. An 89.2 percent reduction from current emission levels attributable to COG combustion at the Youngstown plant will be required. This could be achieved by coke oven gas desulfurization and efficient sulfur recovery.

More effective COG desulfurization permits less efficient sulfur recovery units. This point is illustrated in Figure 2. If the coke oven gas is desulfurized to the 40 grains H_2S /100 scf level corresponding to an H_2S absorption efficiency of 91.4 percent, then an efficiency of 97.6 percent is required in the sulfur recovery unit. However, if the COG is desulfurized to 10 grains/100 scf, (97.8 percent absorption) a sulfur recovery efficiency of only 90.3 percent is required. The relative cost of high efficiency sulfur recovery versus high efficiency COG desulfurization will vary with the control system and therefore the optimum absorption and recovery efficiency will vary. Requests for quotations on a turnkey installed battery limit plant were submitted to COG desulfurization equipment manufacturers based on the following process specifications in addition to the proposed regulation.

A facility for hydrogen sulfide removal from the Campbell Works' coke oven gas will be designed on the following basis.

- The system will include an H_2S absorbing unit and a sulfur recovery plant for removal of sulfur from the scrubbing media.

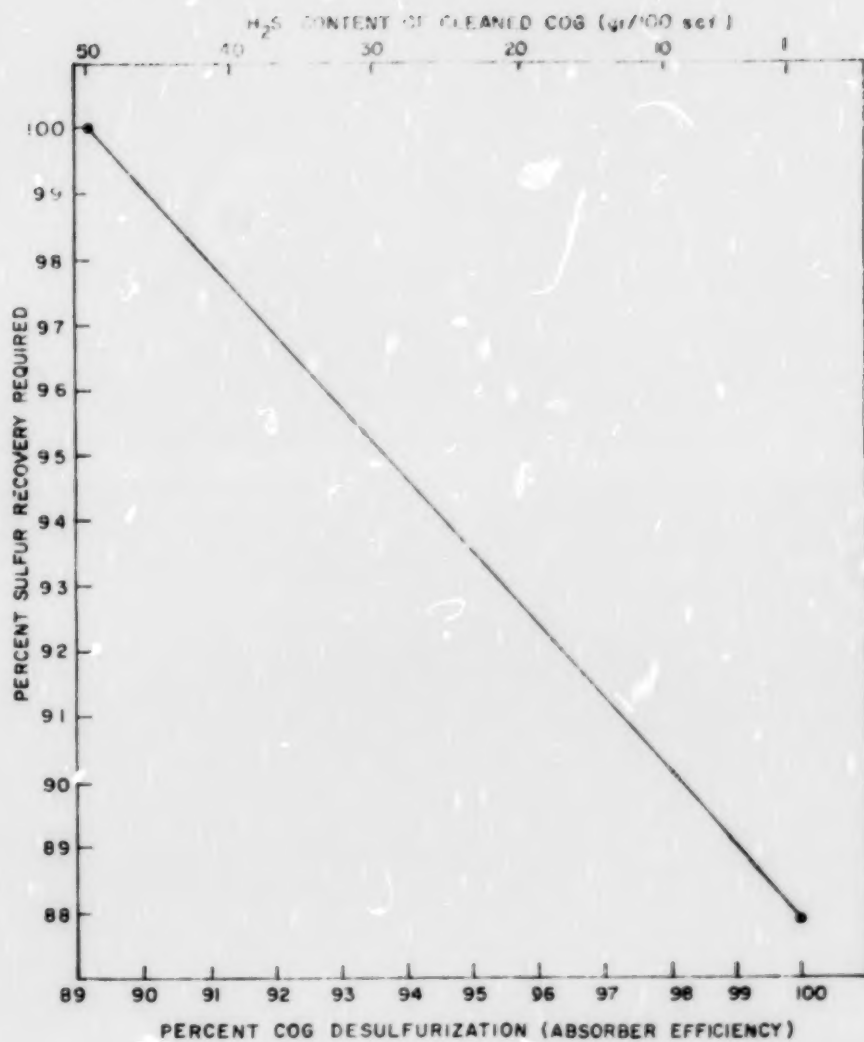


Figure 2. COG desulfurization and sulfur recovery required to meet the proposed 50 grains H₂S/100 scf standard based on an inlet concentration of 464 grains H₂S/100 scf

- Coke oven gas production: 60,000,000 scf per day.
- Maximum volumetric flow rate: 3,000,000 scf per hour.
- Chemical composition (dry basis) of coke oven gas at absorber tie-in after by-product recovery system

Constituent	Volume percent
H ₂ S	0.7
H ₂	52.2
CH ₄	28.9
CO	5.3
N ₂	5.1
Illuminants	3.4
O ₂	2.3
CO ₂	1.8
HCN	60 gr/100 scf
COS	no data available
CS ₂	no data available

- Moisture content: saturated.
- Temperature at absorber tie-in: 21°C.
- Pressure at absorber tie-in: 47 cm WG.
- The following utilities shall be available from YS&T Co. existing sources:
 1. Coke oven gas at 5 PSIG.
 2. Steam at 175 PSIG and 500°F.
 3. Steam at 20 PSIG and saturated.
 4. Electric power, any specified voltage.
 5. Make-up water at any specified quality.
- Cooling water shall be recirculated with cooling towers included.
- Compressed air must be furnished by new compressors to be furnished with plant.

- Auxiliary facilities containing moving parts such as pumps shall be furnished with 100 percent installed backup capacity.
- Heat exchangers, combustion units, and any other required stationary equipment shall be installed in banks such that the loss of one will result in 67 percent capacity still remaining.
- Available space has been indicated on plant drawing shown in Figure 3.

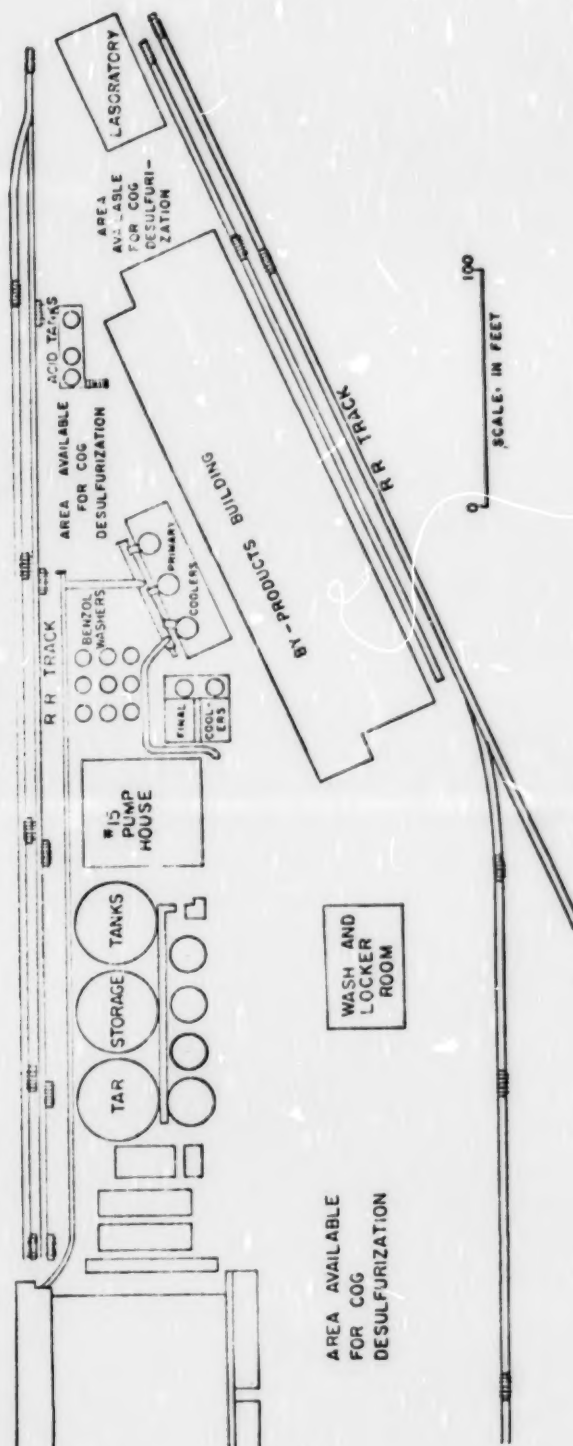


Figure 3. Y&T by-product plant site layout diagram indicating available space for COG desulfurization

SECTION III

CONTROL TECHNOLOGY FOR COKE OVEN GAS DESULFURIZATION

The Vacuum Carbonate, Sultriban, Firma Carl Still, and Stretford processes are commercially available in the United States and are currently operating on North American coke ovens. In addition the Diamox process is reported to be available² and the Takahax process may be available in the near future.³ These processes are technically capable of achieving the proposed sulfur emission limitation of 50 grains H_2S equivalent/100 scf. A few of the systems may be able to achieve 10 grains H_2S /100 scf.

Coke oven gas desulfurization units are operating at eight United States plants, under construction at three plants and committed to construction at two plants as illustrated in Table 2. These 13 plants represent a reasonably large fraction of the 62 United States coke oven plants.⁸ Comparison of the clean coke oven gas production capacity of 322,000 10^6 scf/year in Table 2 to the 1973 industry wide production of 995,000 $\times 10^6$ indicates that up to 1/3 of coke oven gas is currently cleaned. This is a good indication that coke oven gas desulfurization is technically and economically feasible. At this time the Vacuum Carbonate, Sultriban, Firma Carl Still and Stretford process have the most operating experience in North America. These processes are emphasized in the following discussions.

Table 2. INVENTORY OF U.S. COKE OVEN GAS DESULFURIZATION PLANTS, MAY 1976^a

Plants in operation ^b	Location	Gas production 10 ⁶ scf/day	Process
Bethlehem Steel Co.	Burns Harbor, Ind. Lackawanna, N.Y. Sparrows Point, Md. Bethlehem, Pa.	120 50 100 100	Vacuum carbonate Vacuum carbonate Vacuum carbonate Sulfiban
Donner Hanna Coke Co.	Buffalo, N.Y.	30	Vacuum carbonate
National Steel Co.	Weirton, W.Va.	70	Vacuum carbonate
United States Steel Co.	Clairton, Pa.	40	Vacuum carbonate
Inland Steel Co.	Indiana Harbor, Ind.	50	Vacuum carbonate
Shenango, Inc.	Pittsburgh, Pa.	32	Sulfiban
<u>Under construction</u>			
Armco Steel Co.	Middletown, Ohio	60	Firma Carl Still
Jones and Laughlin	Pittsburgh, Pa.	80	Sulfiban
<u>Commitments for construction</u>			
Bethlehem Steel Co.	Franklin, Pa.	60	Sulfiban
Wheeling-Pittsburgh Steel	Follansbee, W.Va.	90	Firma Carl Still

^aReferences 4, 5, 6, 7.

^bDominion Foundry and Steel Ltd., Hamilton, Ontario, Canada operates a 42 x 10⁶ scf/day Stretford system.

LIQUID ABSORPTION PORCESS

The four liquid absorption processes, Vacuum Carbonate, Sulfiban, Firma Carl Still and Diamox involve similar unit operations. Raw COG is cleaned by absorption of acid gases in Na_2CO_3 , monoethanolamine, ammonia, and ammonia respectively. Steam is then used to strip the acid gas from the absorbing medium thus regenerating the absorbent. Particularly in the Vacuum Carbonate system, higher H_2S collection efficiencies required large increases in steam consumption to regenerate a clean absorbent. Claus plants have generally been used for sulfur recovery but a couple of newer systems use or will use sulfuric acid plants. HCN must be destroyed before the sulfur rich gases enter the recovery plant to prevent corrosion and plugging problems.

Vacuum Carbonate Process

As shown in Table 2, the Vacuum Carbonate process is the most widely used COG desulfurization method. Currently this process is employed at 7 plants to clean 450×10^6 scf/day of raw COG. The Vacuum Carbonate process has been marketed by Koppers* since the mid 1950's. Na_2CO_3 is used in this liquid absorption system to collect acid gases. Originally the process was designed to achieve 50 grains $\text{H}_2\text{S}/100$ scf (90 percent absorption of a 500 grains $\text{H}_2\text{S}/100$ scf raw gas) but recent modifications are reported to provide higher efficiencies.⁹

Acid gases collected by the Na_2CO_3 solution are stripped under a slight vacuum and transferred to the sulfur recovery unit. As discussed in the previous section, a 500 grains $\text{H}_2\text{S}/100$ scf raw gas must be desulfurized to below 50 grains $\text{H}_2\text{S}/100$ scf or a 100 percent efficient sulfur recovery unit would be needed. Since 1972-1973, Koppers has offered a system capable of 93 percent absorption but at substantially increased steam and utility costs.⁹ An example process flow sheet of

*Koppers Company, Inc. Piitsburgh, Pennsylvania 15219.

the above process is presented in Figure 4. A two stage system, tested on a pilot scale, is also available that includes design modifications and that reportedly can achieve 10 grains H_2S /100 scf.^{9,10}

HCN has caused Claus plant operating problems. This is common to all COG desulfurization systems and solutions to this problem are discussed later.

Two liquid waste streams result from operation of the vacuum carbonate process. Absorbing solution is normally recycled but based on operating experiences must be replaced every 8 to 36 months.⁴ Condensates from the ejector jets containing dissolved H_2S , HCN, etc., are also a potential liquid waste problem. These acid gases may be stripped from the condensate and returned to the raw COG.

Sulfiban Process

The Sulfiban process, developed by Bethlehem Steel Corporation and Black, Sivalls and Bryson* and marketed by the latter organization, is being utilized at two plants and two units are under construction at other plants. This is a relatively new process with full scale units in operation for less than 3 years. An alkanolamine solution (13 to 18 percent monoethanolamine) is used as an absorbent in this liquid absorption process. Sulfiban pilot units have demonstrated a clear capability to clean COG to 10 grains H_2S /100 scf or less.⁴ Commercial operation has substantiated the pilot plant results. The Shenango plant has operated at absorption efficiencies in the high 90 percent range.¹¹ The Bethlehem Pennsylvania plant, designed to process 100 million scf/day of raw COG containing 325 to 375 gr H_2S /100 scf, has sweetened COG to a 4 to 6 gr H_2S /100 scf level.¹² Figure 5 is a flow diagram of the Sulfiban system operating at Bethlehem including a four-reactor Claus sulfur recovery unit.

* Black, Sivalls and Bryson Process Systems, Inc.
Industrial Products Division
P.O. Box 1948
Oklahoma City, Oklahoma 73101.

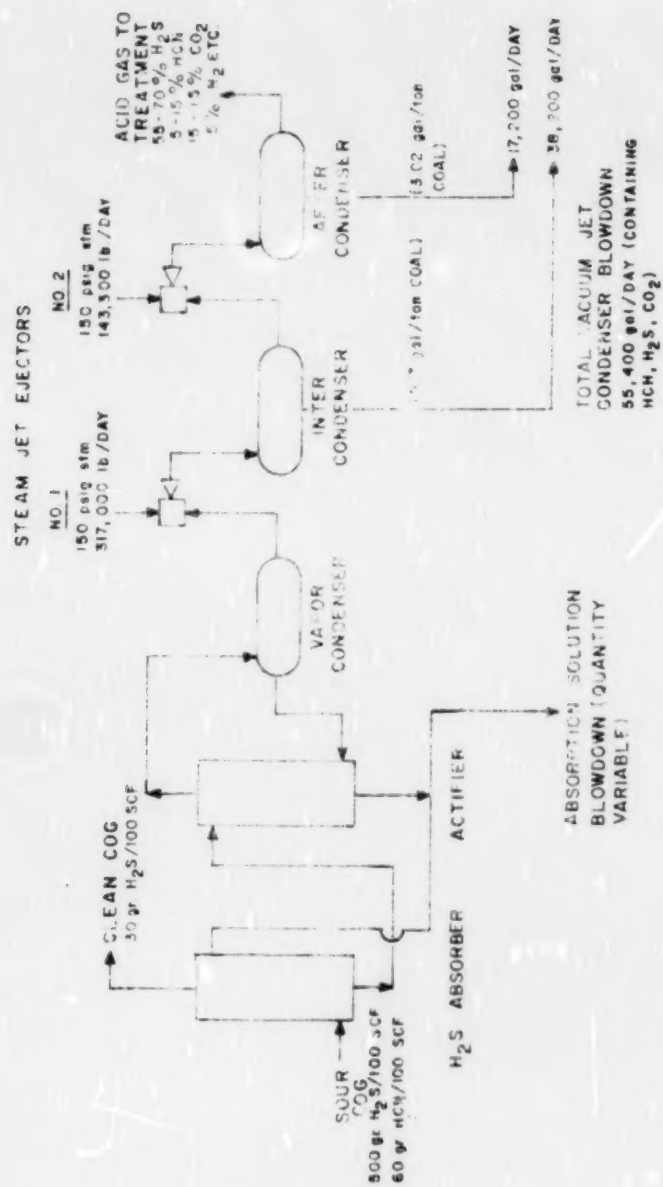


Figure 4. Process flowsheet: Vacuum Carbonate process based on 60 million scf/day COG and 93 percent sulfur collection efficiency⁴

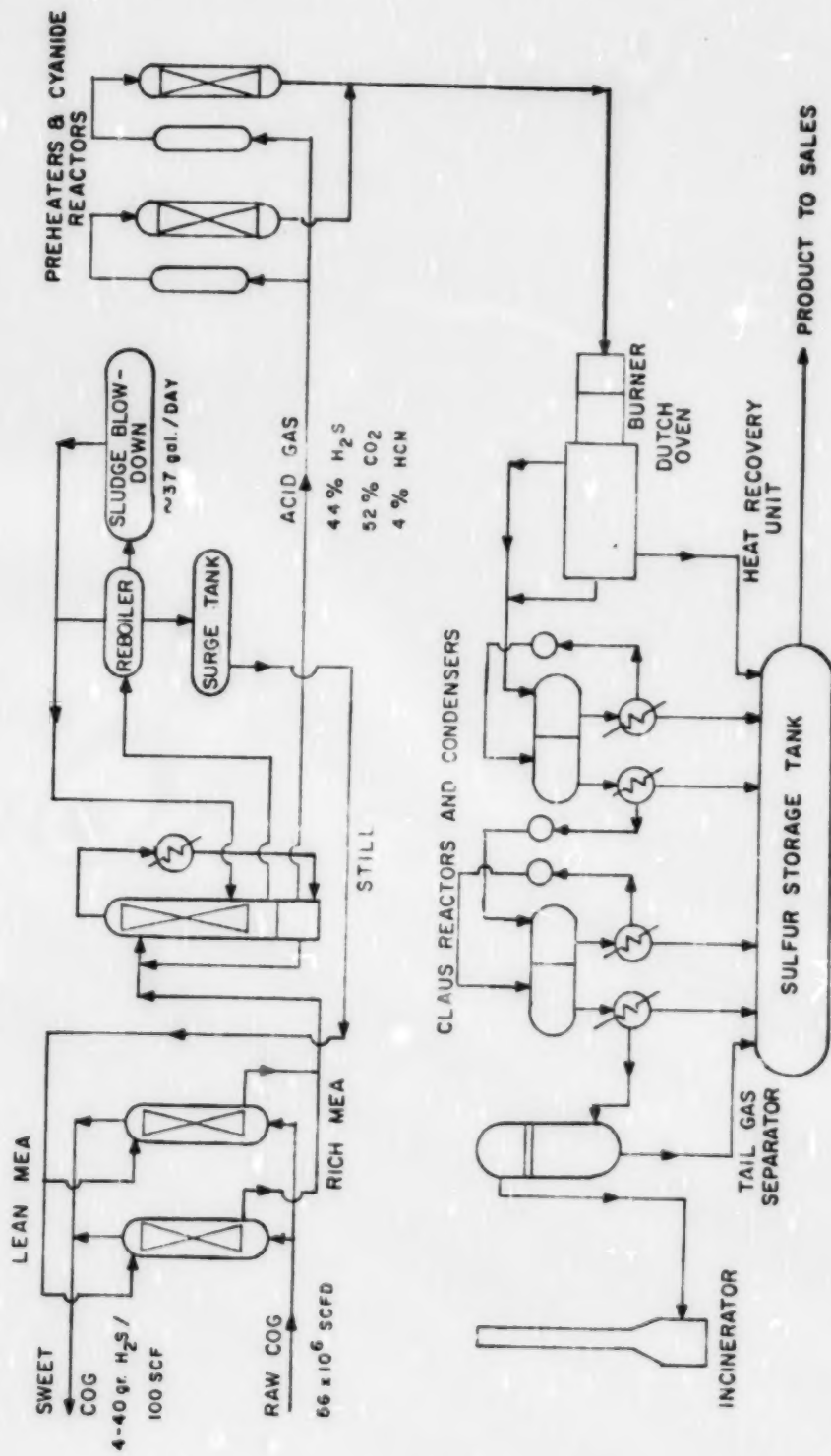


Figure 5. Process flowsheet: Sulfiban process including Claus plant sulfur recovery¹²

The degree of desulfurization is dependent upon the monoethanolamine (MEA) solution circulation rate, the temperature of the solution, and the re-boiler steam rate.¹² Table 3 indicates the degree of desulfurization as a function of MEA circulation rate. Higher desulfurization levels increase the steam requirement for regenerating the amine solution. The steam requirement for desulfurizing to a 10 gr H₂S/100 scf level is approximately double that required for a 50 gr H₂S/100 scf level.⁴

Table 3. COKE OVEN GAS DESULFURIZATION AS A FUNCTION OF AMINE CIRCULATION RATE¹²

COG Flow: 56 x 10 ⁶ scfd Contactor Inlet Temperature: 75-80°F Raw COG Loading: 325-375 gr H ₂ S/100 scf			
Amine circulation rate, gpm	Sweetened COG loading, gr H ₂ S/100 scf	Acid gas composition	
		% H ₂ S	% CO ₂
400	4-6	43.6	52.6
350	5-15	--	--
300	15-20	44.0	52.0
280	20-25	--	--
250	25-30	44.4	51.2
200	30-40	--	--

An advantage of amine desulfurization utilized in the Sulfiban process is the simultaneous removal of organic sulfur. This can be important since the proposed emission regulation limits total sulfur content expressed as H₂S equivalent. Typical organic sulfur content of raw COG at the Bethlehem plant ranged from 3 to 8 gr (H₂S equivalent)/100 scf or less.¹² The Sulfiban process is the only liquid absorption process which removes organic sulfides from the COG stream.

The amine absorption system also has an inherent but minor disadvantage when compared to sodium carbonate absorption. The MEA solution absorbs more CO₂, thus producing an acid gas containing a substantially higher CO₂

concentration. The result is higher production of organic sulfur compounds in the Claus plant combustor. However, these compounds can be efficiently converted to elemental sulfur by modification of the first catalytic converter and switching to a more active catalyst. The cost increase is minor.

As the MEA solution cycles through the system, small quantities of thermally stable compounds such as ferrocyanide and formamide are formed. To prevent the build-up of these compounds, a purge stream is sent to a reclaimer where the MEA is recovered by distillation and the residue is discarded.¹² This sludge contains FeS, prussian blue, thiourea, etc. Approximately one barrel per day of sludge is produced from a plant processing 60 million scf/day of COG. Mixing the sludge with sinter plant feed is one disposal method which has been utilized.⁴

As with the Vacuum Carbonate system, an HCN treatment facility is necessary to prevent Claus plant operating difficulties. This facility will be discussed in a later section.

Firma Carl Still Process

Firma Carl Still has developed this COG desulfurization system to a high degree of sophistication in Germany.⁹ Dravo Corporation* is currently marketing this system in the United States as the Dravo-Still process. The first United States system is expected to start up in mid-1976 at Armco Steel Co., in Middletown, Ohio. A commitment for construction has been made by Wheeling-Pittsburgh Steel for a 90×10^6 scf/day plant.⁵ The Dravo-Still system is an ammonia based liquid absorption process capable

* Dravo Corporation
Engineering Construction Division
One Oliver Plaza
Pittsburgh, Pennsylvania.

of cleaning COG to 10 grains H_2S /100 scf. A process flow diagram for a typical Dravo-Still system is presented in Figure 6.

Desulfurization capability increases with increasing NH_3 concentration. Ammonia based absorption systems are also sensitive to temperature with effectiveness decreasing as temperature increases. This appears to be the reason why a precooler is needed, and 60 to 70°F cooling water is required. At some plants a chiller will be needed during the summer to meet the cooling water criteria. The Dravo-Still system is capable of collecting high percentages of H_2S but total desulfurization is limited by organic sulfur compounds (usually 5 to 10 grains/scf) which are not adsorbed.

Dravo proposes to eliminate Claus plant tail gas by a catalytic reduction furnace. Unconverted SO_2 and H_2S in the tail gas pass to the catalytic furnace where a small amount of coke oven gas is burned with a deficiency of air. This reduces all sulfur compounds back to H_2S . The resulting gas is cooled and recycled back to the H_2S absorber. This recycle lowers the heating value of the COG by 10 to 12 Btu/scf but eliminates all gaseous discharge to the atmosphere.

Waste water from the ammonia still is the only liquid effluent. This waste stream can be combined with the normal by-product plant waste ammonia liquor.

Diamox Process

The Diamox process is an ammonia-based liquid absorption system being marketed in the United States by Mitsubishi Chemical.* Successful

* Mitsubishi Chemical Industries Limited
277 Park Avenue
New York, New York

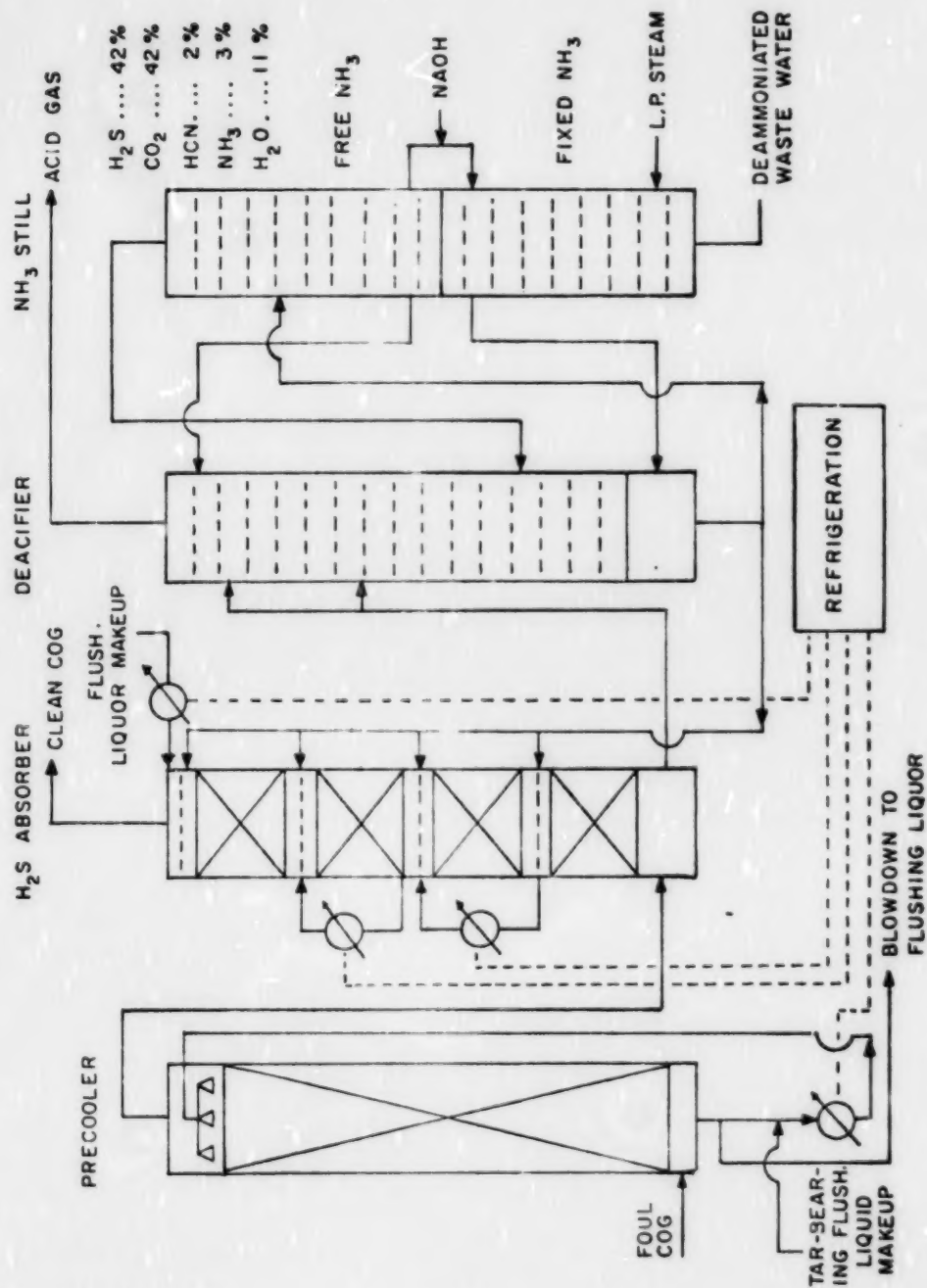


Figure 6. Process flowsheet: Dravo-Firma Carl Still process for COG desulfurization (basis: 35 to 50 grain H₂S/100 scf outlet loading)⁹

operation has been demonstrated in Japan on a 250×10^6 scf/day plant. H_2S content of the clean COG is reported to be 8 grains/100 scf.²

HCN Treatment for Liquid Absorption Processes

HCN in the acid gases from liquid absorption processes must be treated before sulfur recovery. Corrosion and plugging of Claus plants due to HCN has been a serious problem area. This area has been responsible for most of the reliability and technological problems associated with liquid absorption systems for COG desulfurization. Concentrations of HCN should be below 1 percent for successful operation of normal Claus sulfur recovery systems.

Water washing is the oldest applicable method of HCN removal and was utilized by Koppers on a Vacuum Carbonate system in the late 1940's.⁴ After HCN is absorbed it must be recovered as a product or stripped from solution and incinerated. Most steel plants will not be interested in recovering HCN and the costs of stripping and incineration will limit the applicability of this process.

Bethlehem Steel Corporation in conjunction with Black, Sivalls, and Bryson has developed a process incorporating a cyanide destruct reactor to eliminate HCN problems in the operation of Claus plants. Acid gases are preheated, then sent to the reactor where they are blended with a small quantity of air in the presence of a bauxite catalyst.¹² The following series of reactions results in the elimination of hydrogen cyanide.¹³



The HCN is destroyed by oxidative sulfurization and by hydrolysis. For each mole of hydrogen cyanide destroyed, one mole of ammonia is produced. Concentrations of carbon dioxide, carbon monoxide, and organic sulfides also increase. Typical compositions of acid gas streams before and after the cyanide destruct reactor are shown in Table 4.

Table 4. TYPICAL ACID GAS COMPOSITIONS ACROSS CYANIDE DESTRUCT REACTOR FOR VARIOUS ABSORPTION PROCESSES

Component	Amine or ammonia absorption process ¹²		Sodium carbonate absorption process ¹³	
	Cyanide reactor INLET concentration mole %	OUTLET mole %	INLET mole %	OUTLET mole %
H ₂ S	42.3	36.0	79.0	65.4
CO ₂	51.6	48.3	10.5	12.0
HCN	4.4	0.2	7.8	0.2
O ₂	-	-	-	-
N ₂	-	6.9	-	6.9
CS ₂	0.4	0.7	-	0.6
COS	-	1.3	-	2.0
CO	-	0.6	-	1.2
NH ₃	-	3.7	-	6.6
H ₂	-	1.4	-	2.6
Other	1.2	1.1	2.7	2.4

Since ammonia and organic sulfides are major sources of Claus reactor inefficiency, the following modifications in the Claus unit and operation are required. The burner/oven temperature must be maintained at greater than 1900°F by adding fuel gas as necessary. This causes the pyrolytic decomposition of ammonia to nitrogen and hydrogen. The first catalytic

reactor in the Claus unit must be modified to convert organic sulfides to sulfur. A more active catalyst is also necessary.

A full scale cyanide destruct unit and modified Claus unit has proven effective at Bethlehem Lackawana plant. Hydrogen cyanide concentration has been reduced from 16.1 percent to 0.2 percent, and corrosion problems due to HCN have been eliminated.¹³ BS&B is currently marketing this system as an integral component of their Sulfiban process. However, the cyanide destruct system can be used with other liquid absorption processes. In fact, BS&B has a commitment for construction of an HCN destruct unit and Claus plant on a Vacuum Carbonate system at Inland Steel, Indiana Harbor Works.⁷

A catalytic cracking process for decomposing HCN has been developed by Firma Carl Still and utilized in Germany with success.⁹ This system operates at 1500 to 2000°F and is incorporated as part of a modified Claus furnace. The HCN is cracked to $H_2 + CO + N_2$, and any traces of NH_3 remaining in the acid gas stream are also converted to $N_2 + H_2$ as in the Sulfiban system. Dravo is marketing this system as part of the Dravo-Still process in the United States.

A fourth approach has been investigated by Koppers. This modification of the Claus plant combustion chamber to improve HCN incineration was installed on a Vacuum Carbonate system,⁴ Bethlehem Steel Corp., Burns Harbor, Indiana.

WET OXIDATIVE PROCESS

Wet oxidative processes, such as the Stretford and Takahax, differ from liquid absorption systems in that H_2S is oxidized to elemental sulfur while still in the absorbing medium. Elemental sulfur is then simply recovered, without a Claus plant, by filtration. In this type of system the steam consumption is greatly reduced, about 80 to 90 percent, as the stripping step is eliminated. In addition capital costs may be lower since a Claus plant or a sulfuric acid plant is not needed. However, HCN

is a very serious problem for these systems and must be removed before it enters the absorber or consumption of the expensive chemicals will be excessive.

Holmes-Stretford Process

The complete Holmes-Stretford process now being marketed by Wilputte* in the United States uses the Holmes process for treatment of liquid waste streams resulting from HCN absorption and the Stretford wet oxidative system for H_2S absorption. Dominion Foundry and Steel Ltd., in Hamilton, Ontario, Canada is the only plant in North America using the Stretford process. They have ordered a Holmes fixed salt recovery system for treatment of the liquid waste stream.¹⁴

A process flow sheet for the Stretford process is presented in Figure 7. Vanadium, anthraquinone disulfonic acid, anhydrous citric acid, and Na_2CO_3 are circulated through the absorber. After H_2S is dissolved in the liquid it is oxidized to sulfur as the vanadium is reduced from its pentavalent form to its quadrivalent state. The anthraquinone disulfonic acid is employed as an oxidant to regenerate the vanadium to the pentavalent state. During this reaction, the anthraquinone is reduced to semiquinone which is reoxidized back to anthraquinone with air. This absorption oxidation system is capable of achieving H_2S removal efficiencies of over 99 percent. There is no tail-gas; thus overall sulfur removal efficiency is primarily a function of the concentration of organic sulfides in the COG.

The chemical reagents used in the Stretford process react irreversibly with HCN to form thiocyanates and other salts. This increases the amount

* Wilputte Corporation
152 Floral Avenue
Murray Hill, N.J. 07974

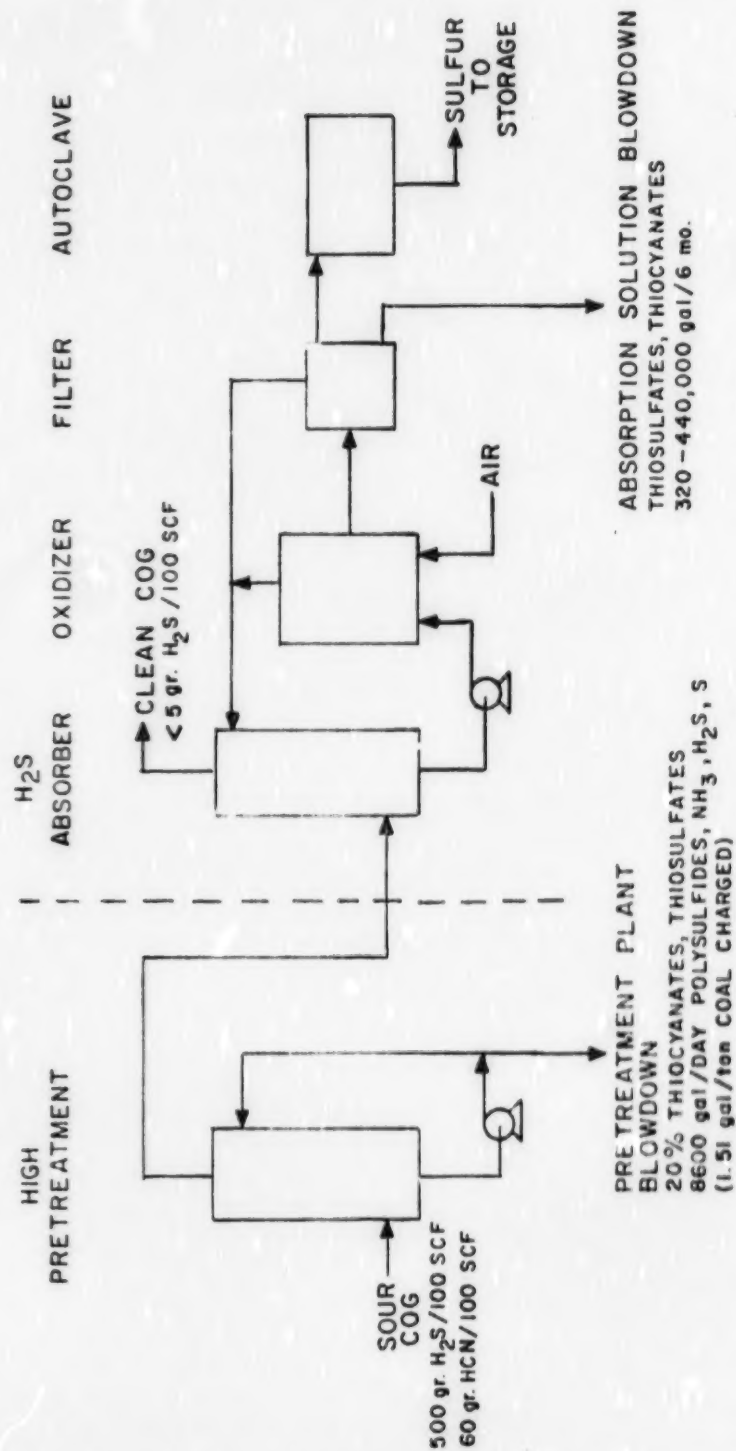


Figure 7. Process flowsheet: The Stretford Process⁴

of blowdown needed and the make-up chemicals required. Besides increasing the quantity of waste from the process, chemical costs can be prohibitive (anthraquinone disulfonic acid costs about \$5/lb). HCN must therefore be removed before the absorber.

Dominion Foundry is using a polysulfide pretreatment system with an ammonia absorbent. Dominion has been able to achieve a 90 percent cyanide removal efficiency, and higher removal efficiencies may be possible using a sodium-based absorbent¹⁴ Wilputte is currently using sodium carbonate in their pretreatment systems. The reactions within the system proceed as follows:



(formation of polysulfides)



(destruction of cyanide)



(regeneration of polysulfides)

The reactions are carried out by passing the COG countercurrent to the sodium polysulfide wash liquor in a scrubbing tower. A sidestream of the circulating liquor is withdrawn and passed through the polysulfide regenerator. A blowdown stream purges reacted salts.

The major problem with the Stretford process is the large quantity of liquid waste containing high concentrations of thiocyanates, polysulfides, thiosulfates, etc. This problem has limited the application of the Stretford system up to this time. These wastes can reportedly be treated by the Holmes process in which the effluent is incinerated in a refractory-lined furnace under proprietary conditions. The products are recycled,

and there are no effluent streams. The first full-scale system began operation at the British Steel Corporation Orgreave Works in July, 1975. After the initial start-up and shakedown period, the fixed salts recovery system reportedly has worked well.¹⁹ Although Dominion Foundry has contracted to purchase a Holmes system, the technical feasibility remains to be commercially demonstrated in North America.

Takahax Process

The Takahax process is similar to the Stretford process except that the oxidizing solution is an alkaline solution of 1,4 naphthaquinone, 2 - sulfonate sodium. H_2S removal efficiencies are also very high, above 99 percent.³ This system is reportedly used on over 30 coke plants in Japan. HCN problems with the Takahax process should be similar to those encountered with the Stretford process.

SECTION IV

COST OF CONTROL SYSTEMS

To obtain accurate control equipment costs GCA asked four manufacturers to update and modify quotations submitted to YS&T in late 1973 and early 1974. The newly proposed regulation and COG flow surges were included in the request for modified cost quotations as well as the other process conditions discussed in Section II. Wilputte; Black, Sivals and Bryson; and Dravo provided complete data for the Holmes-Stretford, Sulfiban, and Dravo-Still processes, respectively. Koppers stated that due to new technology, new pricing, and operating and delivery situations, a new project for their Vacuum Carbonate system would need to be prepared, at an unspecified cost to GCA.* Therefore, an estimate for the Vacuum Carbonate system is not included. Based on the limited available data, the cost of the Vacuum Carbonate system would appear to be similar to or above the Sulfiban system.

The Holmes-Stretford system appears to be the least expensive system. Capital cost of the battery limits plant for the Holmes-Stretford¹⁵ system was \$7.5 million compared to \$10 million for the Sulfiban¹⁶ system and \$9.5 million for the Dravo-Still system.¹⁷ Net operating costs were also considerably lower. In addition the annualized cost which includes cost of capital, federal income tax, depreciation and net operating cost was calculated to be \$1,965,000 for the Holmes-Stretford system and \$2,889,000 for the Sulfiban system and \$2,673,000 for the Dravo Still system. Average annual control costs were calculated to range from \$0.15/lb S removed to

* Koppers also declined to supply copies of a December 1975 proposal made for Republic Steel, Cleveland Works, even though these costs should have been reasonably up-to-date.

\$0.24/lb S removed which is considerably lower than the reported flue gas desulfurization costs for industrial boilers of \$0.2 to \$0.35/lbs (1973 basis - probably much higher now).¹⁸ It should be noted that GCA's evaluation of the three systems for application to Republic Steel Cleveland Works indicated a much narrower cost range of \$0.18 - \$0.20 per pound of sulfur removed. Utility, material, and labor requirements, cost of these requirements and total system costs are discussed in detail in the following sections.

It is not possible to select a single "best" system simply on the basis of the reported cost. Demonstrated performance and reliability, or lack of same, must be weighed against cost disadvantages or advantages by individual equipment purchases. Further, raw material and energy cost and availability must also be considered. Excess steam capacity, on-site electric generating capacity or low cost fuel availability at a specific site could lower energy costs and change the economic analysis. Variations in raw coke oven gas analysis might also change the costs. The three systems discussed in this section are commercially available and can achieve the 50 grains H₂S/100 scf limit. The final system selection is a decision that must be made by the equipment purchaser.

UTILITY, MATERIAL AND LABOR REQUIREMENTS

Detailed utility, material and labor requirements based primarily on data furnished in equipment vendor estimates submitted to GCA are presented in Table 5 for the plant specifications previously presented on page II-5. Each estimate includes a cooling tower; hence, the electrical power requirements in Table 5 include cooling tower operations. Cost of supply water is negligible. Because steam is used primarily for stripping, the Holmes-Stretford process which does not involve stripping uses only 10 percent of the steam quantities used by the other two systems. Small amounts of coke oven gas are used for Claus plant tail gas treatment by the Dravo-Still system and for the Holmes liquid effluent treatment system.

Table 5. UTILITY, MATERIAL AND LABOR REQUIREMENTS FOR 60×10^6 scfd COG DESULFURIZATION SYSTEMS

	Holmes-Stretford	Sulfiban	Dravo-Still
Utility			
Power, kwh/day	29,760	10,920	24,168
Steam, 1000 lb/day	68.9	672	624
Water, gal/day	b	b	b
Coke oven gas, 10^6 scfd	0.40	0.275	0.06
Material			
Vanadium, lb/day	2.9	-	-
Anthraquinone disulfonic acid, lb/day	27.2	-	-
Anhydrous citric acid, lb/day	101.0	-	-
Monoethanolamine, gal/day	-	100	-
K-437 inhibitor (Tretalite) gal/day	-	2	-
Maintenance, percent of fixed capital investment/yr ^c	1.5	1.5	1.5
Labor			
Chemical operator, men/shift	1	1	1
Chemist ⁴ hr/day	2	2	2
Maintenance, percent of fixed capital investment/yr ^c	1.5	1.5	1.5

^aBased primarily on vender quotes to meet the proposed 50 grains H₂S/100 scf regulation.

^bNot significant, cooling tower included in capital and operating costs.

^cGCA assumption, similar to estimates used by Massey^{4,9} and Choi, et al.¹⁸ for industrial pollution control processes.

Materials are used for absorption, oxidation-reduction and maintenance. Chemical consumption was reported by the equipment vendors. In the Holmes-Stretford process chemical consumption depends strongly on the HCN concentration. The reported chemical consumption figures are based on an inlet HCN concentration of 60 to 75 grains/scf and use of the Holmes system to recycle the vanadium. Monoethanolamine is used as the absorbent in the Sulfiban system and is lost in the sludge blowdown and carryover from the stripper. A small quantity of K-437 inhibitor (Tetralite) is also used in the monoethanolamine as a corrosion inhibitor. Net consumption of ammonia in the Dravo-Still system was reported to be negligible. In the absence of hard data on maintenance materials, the cost was assumed to be 1.5 percent of fixed capital investment per year in line with costs used by Massey^{4,9} and Choi, et al.¹⁸

The equipment vendors reported that one chemical operator per shift is required. Labor requirements for a chemist are reported to be 2 hours/day⁴ and maintenance labor is assumed to be equal to the cost of maintenance materials.

UTILITY, MATERIAL, AND LABOR COSTS

Table 6 presents detailed utility, material, and labor costs derived from the requirements noted in Table 5 and the unit costs in Table 6. Total utility, material and labor cost for the example 60×10^6 scfd COG plant are much lower for the Holmes-Stretford system (\$1,990/day) compared to the Sulfiban (\$3,168/day) and the Dravo-Still system (\$2,883). The major reason for the difference is that steam costs for the Holmes-Stretford system are only \$138/day compared to \$1,344/day and \$1,248/day for the other two systems. The bases for the unit costs used for the estimates are noted in Table 6.

Table 6. UTILITY, MATERIAL AND LABOR COSTS FOR 60×10^6 scfd COG DESULFURIZATION SYSTEMS AT YS&T, \$/DAY^a

	Holmes-Stretford	Sulfiban	Dravo-Still
Utility			
Power, \$0.02/kWh ^b	595.2	218.4	483.4
Steam, \$2.0/1000 lb ^c	137.8	1,344.0	1,248.0
Coke oven gas, \$250/10 ⁶ scfd	100.0	68.8	15.0
Total utilities	833.0	1,631.2	1,746.4
Material			
Vanadium, \$5/lb ^e	14.5	-	-
Anthraquinone disulfonic acid, \$5.3/lb ^e	144.2	-	-
Anhydrous citric acid, \$0.50/lb ^e	50.5	-	-
Monoethanolamine, \$0.40/lb ^f	-	333.6	-
K-437 inhibitor (Tretalite), \$4.5/gal ^g	-	8.3	-
Maintenance, 1.5 percent of fixed capital investment/yr	369.9	493.2	464.4
Total material	579.1	835.1	464.4
Labor			
Chemical operator, \$8/hr	192.0	192.0	192.0
Chemist, \$8/hr	16.0	16.0	16.0
Maintenance, 1.5 percent of fixed capital investment/yr	369.9	493.2	464.4
Total labor	577.9	701.2	672.4
Total utility, material and labor	1,990.0	3,167.5	2,883.2

^a For requirements, see Table 5.

^b Ohio Edison, Youngstown, Ohio.

^c Based on the electricity cost and 10 lb steam/kWh.

^d Based on a cost of \$0.5/10⁶ Btu and a heating value of 500 Btu/scf.

^e Wilputte Corporation.

^f Chemical Marketing Reporter, May 1976.

^g BS&B, Process System Division.

CAPITAL AND ANNUALIZED COSTS

Capital costs, annualized costs and the individual components used to compile these costs are presented in Table 7. These costs are current to May 1976. The most important cost component, the installed cost of the battery limits plant, was based on up-to-date quotations furnished by the equipment manufacturers for the Youngstown Sheet and Tube plant.^{15,16,17} Other costs were derived from Tables 5 and 6 as previously described and an accounting method derived from the Utility Financing Method as modified by the Panhandle Eastern Pipeline Company.¹⁸

Capital costs for the Holmes-Stretford system were 20 to 25 percent lower than the other two systems partially due to the fact that a Claus plant is not needed. Similarly net operating costs were \$862,000/year for the Holmes-Stretford system, \$1,400,000/year for the Sulfiban system and \$1,290,000/year for the Dravo-Still system. The average annual cost which includes in addition to the net operating cost, the cost of capital federal income tax and depreciation based on a 20 year expected life ranged from \$1,960,000 to \$2,900,000 corresponding to a control cost of \$0.15 to \$0.24/lb sulfur removed. The cost of these three systems define the range of control cost that may be required to comply with the COG desulfurization regulation. Although in this case the Holmes-Stretford system appears to be the least expensive by a large margin, prospective purchasers must weigh this advantage against the risk of being the first United States facility to use this system.

Table 7. COSTS FOR 60×10^6 scfd COG DESULFURIZATION SYSTEMS
AT YS&T $\$10^3$, MAY 1976

	Holmes-Stretford	Sulfiban	Dravo-Still
<u>Capital requirement</u>			
Battery limits plant installed (BLP) ^a	\$7,500.0	10,000.0	9,500.0
Site preparation and utilities, ^b 20% of BLP	1,500.0	2,000.0	1,800.0
Fixed capital investment (FCI)	9,000.0	12,000.0	11,300.0
Working capital, ^c 20% of gross operating cost	219.2	326.7	300.9
Total capital investment	9,219.2	12,326.7	11,600.9
<u>Annual operating cost</u>			
Labor ^d	210.9	255.9	245.4
Administrative and general overhead, ^c 60% of labor	126.6	153.6	147.3
Utilities ^d	304.0	595.4	637.4
Materials ^d	211.4	304.8	169.5
Local taxes and insurance, ^c 2.7% of FCI	243.0	324.0	305.1
Gross operating cost	1,095.9	1,633.7	1,504.7
Sulfur byproduct, ^c credit \$40/ton	-233.6	-219.0	-219.0
Net operating cost	862.3	1,414.7	1,285.7
<u>Annualized cost</u>			
Annualized capital cost ^f	939.0	1,255.5	1,181.6
Federal income tax ^{c,g}	163.4	219.0	206.0
Net operating cost	862.3	1,414.7	1,285.7
Average annual cost	1,964.7	2,889.2	2,673.3
Average annual control cost, \$/lb S removed	0.150	0.236	0.218

^aManufacturer estimates, May 1976.

^bSite preparation, cost to bring utilities to the battery limit plant, and connect raw COG ducts to battery limit plant based on GCA review of similar costs reported in the literature.

^cBased on Utility Financing Method as modified by the Panhandle Eastern Pipeline Company and described in Reference 18.

^dSee Tables 5 and 6.

^eConservative estimate based on price of \$44/ton currently received by SOHIO for byproduct sulfur.

^fCapital costs are amortized at a discount cash flow rate of 8 percent over 20 years. This method yields an average annual capital cost, including depreciation of 10.18 percent of total capital investment.

^gAverage federal income tax = 1.731 percent of sum of total capital investment and working capital.

SECTION V

REFERENCES

1. McGannon, H.E. (ed.). The Making, Shaping and Treating of Steel. U S Steel. Pittsburgh, Pennsylvania. 1971.
2. Mitsubishi Chemical Industries Limited, Park Avenue, New York, New York.
3. Swaim, C.D. Ford Bacon, and Davis-Takahara Desulfurization Process. (Presented at the 1972 Gas Conditioning Conference. Norman, Oklahoma. March 17, 1972.)
4. Massey, M.J., and R.W. Dunlop. Economics and Alternatives for Sulfur Removal from Coke Oven Gas. J Air Pollu Control Asso. 25(10), October 1975.
5. Personal Communication from Mr. J.A. Anthes of Dravo Corporation. May 1976.
6. Colaianni, L.J. Coke Oven Offgas Yields Fuel, Chemical By-Products. Chem Eng. March 29, 1976.
7. Personal Communication from Mr. Mark Peters of Black, Sivalis & Bryson, Inc. June, 1976.
8. Minerals Yearbook 1973. Volume I: Metals, Minerals, and Fuels. U.S. Bureau of Mines, Washington, D.C. 1975.
9. Massey, M.J., and R.W. Dunlap. Assessment of Technologies for the Desulfurization of Coke Oven Gas. (Presented at the 24th Ironmaking Conference of the AIME. April 15, 1975.)
10. Vajda, F.A. Process Description of Koppers Two Stage Hot Vacuum Carbonate System. October 30, 1975. Unpublished data from Koppers Company, Inc.
11. Personal Communication from Mr. B. Bloom, Division of Stationary Source Enforcement, U.S. Environmental Protection Agency, Washington, D.C. May, 1976.

12. Williams, J.A., and O.A. Homberg. Coke Oven Gas Desulfurization and Sulfur Recovery Utilizing the Sulfiban Process. (Presented at the 35th Ironmaking Conference of the AIME. March, 1976.)
13. Homberg, O.A., and A.H. Singleton. Performance and Problems of Claus Plant Operation of Coke Oven Acid Gases. J Air Pollu Control Asso. 25(4). April 1975.
14. Personal Communication from Mr. J. Plendrith. Dominion Foundry and Steel, Ltd. Hamilton Ontario, Canada. May 1976.
15. Wilputte Corporation Cost Estimate Received from W.E. Carbone. May 1976.
16. Black, Sivalis and Bryson, Process Systems, Inc. Cost Estimate Received from W.M. Peters. May 1976.
17. Dravo Cost Estimate received from J.A. Anthes. May 1976.
18. Choi, P.S.K., E.L. Kropp, W.E. Ballantyne, M.Y. Anastas, A.A. Putnam, D.W. Hissong, and T.J. Thomas. SO₂ Reduction in Nonutility Combustion Sources Technical and Economic Comparisons of Alternatives. Battelle Columbus Laboratories. U.S. Environmental Protection Agency Report, EPA-600/2-75-073. Research Triangle Park, North Carolina. October 1975.
19. Personal Communication with Mr. W.E. Carbone, Wilputte Corporation. May 1976.